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***In situ* reaction mechanism studies of plasma-assisted atomic layer deposition of Al₂O₃**

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Reaction mechanisms during plasma-assisted atomic layer deposition (ALD) of Al₂O₃ from Al(CH₃)₃ and O₂ plasma were studied by time-resolved quartz crystal microbalance measurements, mass spectrometry, and optical emission spectroscopy. Al(CH₃)₃ chemisorption on the oxide surface after the plasma pulse releases CH₄ products while from the detection of CO, CO₂, and H₂O in the O₂ plasma it is established that surface –CH₃ groups are predominantly removed by O radical-driven combustionlike reactions. Also a second pathway exists for –CH₃ removal driven by H₂O generated in this plasma step. These reaction pathways are expected to be generic for plasma-assisted ALD of oxides from metal organic precursors. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357886]

The search for appropriate high-*k* dielectrics for semiconductor applications has made atomic layer deposition (ALD) of oxides a very active research field. Recently, the investigations have been extended to ALD processes in which the commonly used H₂O dosing step is replaced by O₃ dosing or O₂ plasma exposure, because of potential advantages such as improved film quality, increased flexibility in process conditions, and feasibility of lower deposition temperatures. For the pure thermal process, the reaction mechanisms underlying film growth have been investigated for several materials but for the O₃-based or plasma-assisted ALD process virtually no dedicated studies have appeared yet. Especially the thermal process for Al₂O₃ ALD from trimethylaluminum [Al(CH₃)₃] and H₂O, which can be considered as a model system for ALD,¹ has been examined quite thoroughly both experimentally and theoretically.^{2–9} Details about the reaction mechanism have been established for this process, which is ruled by (i) chemisorption of Al(CH₃)₃ on –OH surface groups forming adsorbed (–O–)_nAl(CH₃)_{3–n} by splitting off one of more ligands in the form of CH₄ and (ii) the oxidation of the metal by H₂O regenerating –OH surface groups while forming CH₄.

In this letter, we report on the reaction mechanism of plasma-assisted ALD of Al₂O₃ by Al(CH₃)₃ and O₂ plasma. *In situ* diagnostics such as quartz crystal microbalance and quadrupole mass spectrometry were employed and also optical emission spectroscopy was shown to provide unique time-resolved information. Details of the chemisorption step of Al(CH₃)₃ are presented and key insight about the removal of –CH₃ ligands by the plasma is provided by revealing combustionlike reactions by O radicals. Such reactions have been hypothesized for metal organic precursors earlier, but with-

out experimental support. It is also shown that reaction products created by the plasma (particularly H₂O) can lead to concurrent reaction pathways at the surface and that reaction products can significantly affect the plasma properties.

The experiments were carried out in a remote-plasma ALD system with an inductively coupled plasma source. A continuous flow of O₂ serves both as plasma gas and as purge gas. Al(CH₃)₃ dosing and plasma exposure are alternated by releasing a trapped volume of Al(CH₃)₃ at room temperature and by pulsing 100 W plasma power for 2 s, respectively. During the cycle the background pressure was kept constant at ~10 mTorr and the deposition temperature was set at 70 °C by the wall heating of the reactor. Film growth was monitored by a quartz crystal microbalance (QCM) with a bakeable crystal holder positioned close to the substrate holder. The gold covered quartz crystals were first coated with Al₂O₃ before taking any data. The reaction products were sampled by a differentially pumped quadrupole mass spectrometer (QMS) fitted at the side of the reactor while plasma emission just above the substrate holder was detected by optical emission spectroscopy (OES). All diagnostics were operated simultaneously and their data acquisition rate was set to 10 Hz. In these experiments the intermitted purge times were set as such to allow for a detailed study by the diagnostics. The Al₂O₃ material properties obtained with this experimental setup have been reported.^{10,11}

A typical example of the mass change during the plasma-assisted ALD cycles as measured by the QCM is shown in Fig. 1(a). When pulsing the Al(CH₃)₃ in the reactor, the chemisorption of Al(CH₃)₃ on the surface can be observed as a sharp increase in mass (*m*₁) which takes place within the time resolution of the QCM (100 ms). When the plasma is turned on, first a large negative spike is observed in the QCM signal followed by a recovery of the signal to a slightly higher level in mass (*m*₂) than after Al(CH₃)₃ chemisorption. The spike during plasma exposure can be attributed

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FIG. 1. (Color online) Apparent mass change as determined from the QCM signal for (a) an ALD cycle including $\text{Al}(\text{CH}_3)_3$ dosing and O_2 plasma exposure and (b) only O_2 plasma exposure.

to an artifact caused by the plasma, most probably due to charging of the crystal. The spike is also observed when exposing the QCM just to a plasma pulse as shown in Fig. 1(b); however, in this case the signal returns exactly to its starting level before the plasma pulse. The mass increase after the plasma step, $m_2 - m_1$, can therefore be attributed to the replacement of $-\text{CH}_3$ ligands by oxide surface groups.

From the ratio of the mass increase in the two half reactions, the fraction of ligands released during the $\text{Al}(\text{CH}_3)_3$ pulse can be estimated following the approach proposed by Rahtu and Ritala.¹² In the present case, at 70°C , ~ 1.8 methyl ($-\text{CH}_3$) groups per chemisorbed $\text{Al}(\text{CH}_3)_3$ molecule are released indicating that the $\text{Al}(\text{CH}_3)_3$ mainly binds bifunctionally on the surface creating predominantly $(-\text{O}-)_2\text{Al}(\text{CH}_3)$ surface groups. This is similar to what has been reported for thermal ALD ($150\text{--}350^\circ\text{C}$) by QCM.⁶ Remarkably different is, however, that the growth rate as determined from the QCM measurements ($54\text{ ng cm}^{-2}/\text{cycle}$) as well as from *in situ* spectroscopic ellipsometry ($1.7\text{ \AA}/\text{cycle}$) is much higher than for H_2O ($32\text{ ng cm}^{-2}/\text{cycle}$ or $1.1\text{ \AA}/\text{cycle}$) (Ref. 4) or O_3 ($1.1\text{ \AA}/\text{cycle}$) (Ref. 13) based processes at $\sim 70^\circ\text{C}$. A higher growth rate per cycle has been reported earlier for both remote and direct plasmas,^{14,15} and we attribute this higher growth rate to the availability of a higher number of reactive oxide surface groups for $\text{Al}(\text{CH}_3)_3$ chemisorption after the O_2 plasma.

Figure 2 shows the QMS signal recorded for selected mass-to-charge (m/z) ratios during several ALD cycles. The most likely parent molecules leading to the different signals, which can either be due to direct or dissociative ionization of the corresponding molecule, are indicated. During $\text{Al}(\text{CH}_3)_3$ pulsing, the signal at $m/z=15$ and 16 increases which can be attributed to the detection of CH_4 released during $\text{Al}(\text{CH}_3)_3$ chemisorption at the oxide surface. In principle, also the dissociative ionization of $\text{Al}(\text{CH}_3)_3$ contributes to the signal at $m/z=15$ but it was established that this contribution was negligible under the current conditions in which the amount of $\text{Al}(\text{CH}_3)_3$ dosed is just sufficient to saturate the surface reactions at the substrate and reactor's wall. For high over-exposures of $\text{Al}(\text{CH}_3)_3$, i.e., with a significant amount of gaseous $\text{Al}(\text{CH}_3)_3$ in the reactor, a signal appeared at $m/z=27$ (Al^+) with a minor contribution at $m/z=15$. Furthermore, the relative increase at $m/z=15$ and 16 in Fig. 2 is in good agreement with the cracking pattern of CH_4 in the QMS. It can therefore be concluded that $\text{Al}(\text{CH}_3)_3$ chemi-

FIG. 2. (Color online) Time-resolved mass spectrometry signals for several ALD cycles. The most likely parent molecules contributing to the signals at the selected mass-to-charge ratios m/z are indicated.

sorption at the surface releases $-\text{CH}_3$ groups by a reaction between the $-\text{CH}_3$ and hydrogen at the surface, e.g., by chemisorption of $\text{Al}(\text{CH}_3)_3$ on $-\text{OH}$ surface groups.

During the plasma step, the signals at $m/z=18$, 28 , and 44 increase indicating the detection of H_2O , CO , and CO_2 reaction products. The signal at $m/z=28$ can partly be attributed to dissociative ionization of CO_2 in the QMS, but from the cracking pattern and calibration measurements it has been established that CO is also present in the plasma. From these observations it can be concluded that the $-\text{CH}_3$ groups existing at the surface after $\text{Al}(\text{CH}_3)_3$ chemisorption are removed from the surface by combustionlike reactions. These reactions as well as the oxidation of the Al are predominantly driven by the abundant O radicals in the plasma.¹⁶ This consumption of O radicals affects the O_2 mass balance in the plasma and leads to a reduction of the O_2 signal in the initial phase of the plasma step as can be observed at $m/z=16$ and 32 .

During the O_2 plasma pulse also an increase in the signal at $m/z=15$ is observed. Closer observation of the data reveals that this signal is observed for a significantly shorter duration than the signals at $m/z=18$, 28 , and 44 (about twice as short). We attribute the signal to CH_4 released from the surface by the interaction of H_2O produced by the combustionlike reactions with $-\text{CH}_3$ surface groups. This forms a concurrent reaction path to the combustionlike process once H_2O is produced but only when still a considerable amount of $-\text{CH}_3$ groups is present at the surface. This indirect “thermal ALD” reaction becomes insignificant when the combustionlike reactions have removed most of the $-\text{CH}_3$ groups. It should be noted that the detection of CH_4 at $m/z=16$ is obscured by the consumption of O_2 during the plasma pulse. Furthermore, we were not able to observe the formation of larger hydrocarbons, C_xH_y , in the plasma as, for example, suggested by Elliot *et al.* for the interaction between O atoms and $-\text{CH}_3$ groups.¹⁷

Due to the relatively low pressure in the plasma, it can be assumed that the CO_2 and H_2O observed are predominantly formed by the reaction between O radicals and $-\text{CH}_3$ ligands. The CO in the plasma can, however, be a product from incomplete combustion reactions or be produced in the plasma by electron-impact dissociation of CO_2 . Calibration experiments using plasmas in CO/O_2 and CO_2/O_2 mixtures showed that a significant level of CO is also created in a CO_2 -based plasma. Furthermore, it was determined that the amounts of CO and CO_2 in the initial phase of the O_2 plasma after $\text{Al}(\text{CH}_3)_3$ dosing reach levels of $\sim 7\%$ of the total gas density.

The excitation of the plasma species gives also insight into the plasma-assisted ALD process. In Fig. 3(a) the emis-

FIG. 3. (Color online) (a) Emission from a pure O₂ plasma and an O₂ plasma ignited after a preceding Al(CH₃)₃ dose as recorded in the first 200 ms after the plasma strike. (b) Time-resolved signal of selected emission lines during the O₂ plasma step after a preceding Al(CH₃)₃ dose.

sion spectrum of a pure O₂ plasma is shown. Mainly emission by O₂⁺ from the first ($b^4\Sigma_g^- \rightarrow a^4\Pi_u$) and second ($A^2\Pi_u \rightarrow X^2\Pi_g$) negative systems and by O radicals ($^5P \rightarrow ^5S$, 777 nm and $^3P \rightarrow ^3S$, 845 nm) can be observed. When an Al(CH₃)₃ dose has preceded the plasma exposure, the emission in the first hundreds of milliseconds of the plasma pulse is remarkably different from the pure O₂ plasma. As also shown in Fig. 3(a) there is an intense broadband emission in the first 200 ms of the plasma pulse which can clearly be observed by the naked eye as a “blue flash.”¹⁸ At the end of the plasma pulse the emission is identical to the emission of a pure O₂ plasma. The difference in emission at the start of the plasma pulse can be attributed to the plasma excitation of reaction products released from the surface which evidently disappears when the surface reactions are saturated. From the identification of the spectral lines, we found that the broadband emission is coming predominantly from CO (with the Ångström and Herzberg systems most prominent). Furthermore, also emission by atomic hydrogen (H _{α}) can clearly be observed which is due to electron-impact dissociation of the H₂O and CH₄ reaction products.

Figure 3(b) shows time-resolved emission signals of the reaction products (CO Ångström system $\nu - \nu' = 0 - 2$ and H _{α}) and of the O radicals ($3p^5P \rightarrow 3s^5S$) in the plasma. From the time-resolved signal of H and CO, for which $1/e$ -decay times of ~ 300 and ~ 500 ms can be determined, respectively, it can be concluded that the surface reactions during the plasma step are saturated well within 1 s. This is in agreement with results obtained by *in situ* spectroscopic ellipsometry showing saturation of the growth rate for plasma pulses of >0.5 s. The time-resolved emission from O radicals shows that oxygen is consumed by the surface reactions generating the CO, CO₂, and H₂O reaction products as well as by oxidizing the Al on the surface.

In summary, for the plasma-assisted ALD process of Al₂O₃ it has been established that the O₂ plasma removes

–CH₃ ligands from the surface mainly by combustionlike reactions driven by O radicals although a concurrent thermal-ALD-like reaction path by H₂O generated by the plasma is also present. The subsequent chemisorption step of Al(CH₃)₃ on the surface appears to be similar as for thermal ALD albeit at a higher saturation level. Apparently, after the O₂ plasma exposure a higher number of reactive oxide surface groups are available for Al(CH₃)₃ chemisorption. Whether these oxide surface groups after O₂ plasma exposure are predominantly –OH groups such as in the thermal ALD process cannot be concluded from the present data. However, the release of CH₄ during Al(CH₃)₃ chemisorption indicates the availability of hydrogen at the surface and surface –OH groups are likely to be formed in the reaction by the H₂O created in the combustionlike reactions. The reaction mechanism discussed is expected to have generic relevance for plasma-assisted ALD processes of other oxides from metal organic precursors and the insight presented has important implications for processing, e.g., in terms of growth rate per cycle for plasma-assisted ALD. Furthermore, it is shown that reaction products from the plasma can significantly affect the plasma properties and hardware settings (e.g., power coupling) while a technique such as optical emission spectroscopy yields unique opportunities to study and optimize the properties for plasma-assisted ALD processes.

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- ¹⁸See EPAPS Document No. E-APPLAB-89-331639 for a movie of the plasma emission during a plasma-assisted ALD cycle. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).